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THE COMPOSITION OF THE RED CLAY

F. W. CLARKE

In the volume upon *Deep Sea Deposits*, issued as one of the reports of the "Challenger" expedition, there are published twenty-five analyses of the "red clays."[1] This sediment is now recognized as the most extensive and important of all oceanic deposits, for it covers 51,500,000 square miles of the sea floor and is characteristic of the greatest depths. It is, therefore, obviously desirable to know its average composition as exactly as possible, and for that reason the following investigation was undertaken.

Of the analyses above mentioned 21 were by Brazier, 2 by Hornung, 1 by Klement, and 1 by Renard. They are, however, not strictly comparable, as a glance at the recorded data will show, nor are they, from the point of view of the modern analyst, so complete as they should be. For example, that ubiquitous element, titanium, was not determined in any of the analyses, for at the time they were made, its importance and relative abundance were not appreciated. Other substances, which are common in clays, were neglected for similar reasons, but their significance is now better understood, and improvements in analytical methods have made it easier to search for them. In Brazier's analyses the alkalies were not estimated, but were reported by the other analysts; an omission in the first group that was not due to oversight, but to the limitations of the purposes for which the work was done. The general nature of the red clay was well established, its great variability in composition was clearly shown, and its relations to other clays were made sufficiently plain to satisfy all ordinary requirements.

Of late years, however, it has become a matter of interest to determine the relative abundance and distribution of the chemical elements; and in an inquiry of that sort so notable a substance as the red clay could not well be neglected. A new and more elaborate analysis of it, therefore, seemed to be required, and to that end two methods of investigation were available. First, it was possible to make a number of individual analyses of separate samples, from which an average might be computed. Secondly, one composite sample could be analyzed, giving the desired information once for all. The first method, evidently, would have involved much labor, too much, indeed, to be justifiable. The second method would solve the problem equally well, but with greater ease and vastly less expenditure of time. The second, therefore, was chosen. Through the kindness of Sir John Murray, and his secretary, Mr. James Chumley, fifty-one samples of the red clay, from as many localities, and approximately equal in weight, were combined into a single sample, and that was analyzed by my associates in the laboratory of the United States Geological Survey.[1] The results of the composite analysis will be given presently.

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[1] *Deep Sea Deposits*, pp. 198, 201, 425–35.

The composite sample, as made up by Mr. Chumley, contained 35 samples from the dredgings of the Challenger expedition, 12 collected by the "Egeria," 2 by the "Waterwitch," and 2 by the "Penguin." Of these, 8 samples were collected in the Atlantic, 2 in the Indian Ocean, and 41 in the Pacific. The "Challenger" localities were stations Nos. 5, 9, 26, 27, 29, 160, 165, 181, 215, 221, 226, 228, 229, 230, 238, 240, 241, 244, 247, 251, 253, 254, 255, 256, 258, 259, 275, 277, 285, 286, 288, 294, 329, 330, and 353. These stations can be identified by reference to the published reports of the expedition.[2] The geographic range of the collection is evidently large enough to give a significant average, and the number of individual samples was also adequate. Twelve of the localities enumerated above are represented among the analyses already published in the volume on *Deep Sea Deposits* and are there indicated by their station numbers. The other localities furnished material hitherto unstudied chemically.

The new analysis of the clay was made upon the air-dried and unwashed sample. It, therefore, included adherent sea salts, and hygroscopic moisture, varying in these respects from the earlier analyses. The magnitude of these variations, however, was determined, and appears in the figures given below. The final data are as follows:

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[1] The analytical methods employed were those prescribed by Hillebrand, in *U. S. G. S. Bulletin, No. 305*.

[2] A chart showing the position at which each sample was taken, was also furnished with the material sent for analysis.

A. General analysis, by Mr. George Steiger.
B. Portion soluble in cold water, by Mr. George Steiger.
C. Special determinations, by Dr. W. F. Hillebrand.
D. Special determinations, on material concentrated from 150 grammes of clay, by Dr. E. C. Sullivan.

These last determinations were checked by blank experiments upon equal quantities of the reagents employed in the research.

TABLE I

	A.	B.	C.	D.
SiO_2	45.32	none	BaO.....0.16	CuO.....0.02
Al_2O_3	13.26	none	Cr_2O_3....0.011	PbO.....0.007
Fe_2O_3	7.20	none	V_2O_3.....0.035	ZnO.....0.004
FeO	0.70	none	MoO_3....trace	As_2O_3....0.0007
MgO	3.05	0.21		
CaO	6.82	0.19		
Na_2O	3.63	2.01		
K_2O	2.43			
H_2O at 106°	3.28	....		
H_2O above 106°	5.93	....		
TiO_2	0.82	....		
CO_2	3.91	....		
P_2O_5	0.25	....		
SO_3	0.48	0.39		
Cl	2.77	2.73		
F	none	....		
Cr_2O_3	0.01	....		
NiO, CoO	0.032	....		
MnO_2	1.01	....		
BaO	0.17	....		
SrO	0.046	....		
Li_2O	none	....		
V_2O_3	0.023	....		
	101.141	5.53		
Less $O=Cl$	0.62	0.62		
	100.521	4.91		

Zirconia and the rare earths were sought for by Dr. Hillebrand, but not found. Titanium, chromium, vanadium, barium, strontium, nickel, copper, lead, zinc, arsenic, and molybdenum were not reported in the "Challenger" analyses. Their widespread distribution in the igneous rocks is, however, well recognized. The absence of lithium and fluorine is noteworthy. The unusually high proportion of manganese suggests the presence of disseminated or incipient manganese nodules, like that so admirably analyzed by Gibson.[1] In his work several of the rarer elements were determined; so that their existence in the oceanic sediments is no new discovery. The fact of their general distribution, however, remained to be proved.

In order to establish the true composition of the clay substance, some deductions must be made from the analysis as it is now stated. Hygroscopic water and soluble matter must be eliminated, and also the calcium carbonate which is represented by the CO_2. The composition of the aqueous extract, as given by Mr. Steiger's figures, is very near that of the sea salts. I have therefore taken Dittmar's analysis of sea salts as a standard, and subtracted their equivalent, as measured by the chlorine in the unleached clay, from the analysis of the latter. A slight excess of SO_3 remained, which I have also thrown out as representing gypsum. In short, from the general analysis I have withdrawn the water lost below 106°, the sea salts, the calcium carbonate, and a little gypsum, and recalculated the remainder to 100 per cent.

For comparison, I have combined the twenty-five analyses of the "Challenger" report into an average, from which similar subtractions, so far as they were needed, have been made. In this case only gypsum and calcium carbonate were rejectable. As for the combination, its value is not very great, because of the inequality shown by the individual analyses. Only in four of the latter were alkalies determined, and the mean of those four I have assumed to be representative of all. The ferrous oxide is even more doubtful, for it was only determined in one of Hornung's analyses, and neglected in the others. Still, as will be seen in the subjoined table, the comparison is not without significance, and even if it is not perfect, it is better than none at all.

The minor elements, not shown in the "Challenger" analyses, only sum up, altogether, to 1.36 per cent. Apart from these the comparison is satisfactory in some respects, not so in others. In silica, alumina, and water, the agreement is fairly good, but in iron, the old analyses range much higher than the new. Possibly for the individual analyses, the reddest and therefore the most ferruginous samples were chosen for examination, as being presumably the most typical.

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[1] *Deep Sea Deposits*, pp. 422, 423.

TABLE II

REDUCED ANALYSES

	Composite Analysis	Challenger Average
SiO_2	54.48	54.28
TiO_2	0.98	.....
Al_2O_3	15.94	16.41
Cr_2O_3	0.012	.....
Fe_2O_3	8.66	13.58
FeO	0.84	1.26
NiO, CoO	0.039	.....
MnO_2	1.21	1.62
MgO	3.31	1.76
CaO	1.96	0.74
SrO	0.056	.....
BaO	0.20	.....
K_2O	2.85	1.61
Na_2O	2.05	1.37
V_2O_3	0.035	.....
As_2O_3	0.001	.....
MoO_3	trace	.....
P_2O_5	0.30	0.35
CuO	0.024	.....
PbO	0.008	.....
ZnO	0.005	.....
H_2O	7.04	7.02
	100.000	100.00

On the proximate or mineralogical composition of the red clay, I have no important suggestions to offer. That problem was discussed at some length, in the "Challenger" report, on the basis of Brazier's analyses. In those analyses there was discrimination between the portion of the clay soluble in strong hydrochloric acid and the portion insoluble. In nearly every case the soluble ferric oxide was reported in excess of the insoluble; from which I am inclined to suspect that the iron of the clay is present, at least partially, in limonitic or glauconitic combination. The new, composite analysis shows a quantity of potash which suggests the presence of glauconite. The latter compound may well exist in a diffused form, quite unlike its common granular variety, and therefore not so readily recognized. This is a mere suspicion, not entitled to much weight at present, but worth considering in future investigations. My specific problem has been to study the distribution of the chemical elements in nature, and to that end the composite analysis of the red clay is a step forward.

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ADDENDUM

Since the foregoing pages were written I have received from Sir John Murray a composite of 52 "terrigenous" clays, dredged up from oceanic depths ranging from 140 to 2,120 fathoms. In the nomenclature of the "Challenger" expedition, 48 of the individual samples are classified as "blue muds," and 4 as "green muds." Twenty-three of the clays were collected by the "Challenger;" the others were brought in from voyages of the "Buccaneer," "Dart," "Egeria," and "Rambler." The range of collection, as in the case of the "red clay," was world-wide, and all of the great oceans are represented in the composite sample.

Molybdenum and zirconium were not detected. Nickel, cobalt, lead, zinc, and arsenic, which were reported in the red clay, were not looked for. Apart from these trivial omissions, the red and terrigenous clays are fairly comparable. The red clay is lower in silica and alumina, but higher in iron than the muds, and other minor differences appear. The high manganese of the red clay may be correlated with the abundance of manganese nodules in the greater oceanic depths. The results of analysis appear in the following table:

A. General analysis by Mr. Steiger.
B. Portion soluble in water.
C. Analysis reduced to standard form by rejecting soluble salts, calcium carbonate, and hygroscopic water, and recalculation of the remainder to 100 per cent.

TABLE III

	A.	B.	C.
SiO_2	46.64	.14	57.09
TiO_2	1.04		1.27
Al_2O_3	14.08		17.24
Cr_2O_3	.044		.05
Fe_2O_3	4.14		5.07
FeO	1.88		2.30
MnO	.10		.12
MgO	1.95	.18	2.17
CaO	7.20	.38	2.04
SrO	0.25		.03
BaO	.05		.06
K_2O	1.84		2.25
Na_2O	2.98	2.12	1.05
V_2O_3	.028		.03
P_2O_5	.17		.21
CO_2	4.05		....
SO_3	.32	.32	....
S	.11		.13
Cl	2.25	2.25	....
CuO	.016		.02
C	1.38		1.69
H_2O at 105°	4.73		....
H_2O above 105°	5.86		7.18
	100.883		100.00
Less $O = Cl$	.56		
	100.323		

June 27, 1907